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alumina gels	colloidal particles
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gel particles	

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The process used to form monolithic transparent Al_2O_3 bodies from metal-organic starting materials at low temperature via the gel process involves essentially four steps: hydrolysis, peptization, gel formation, and pyrolysis. Each step has been systematically investigated by modification of associated variables in order to determine the combination of factors which produces optimum results. It has been found that the interparticle distance, that is, the extent of approach attained by colloidal particles, at the point of gelling is of critical importance in

20. ABSTRACT CONTINUED

maintaining monolithicity during the gel-oxide conversion. Minimization of
this distance not only reduces the amount of shrinkage necessary during
liberation of organics, allowing the body to remain in one piece, but also
appears to allow interparticle bond formation during drying and pyrolysis,
possibly involving hydroxyl and alkyl groups. For this reason, the factors that
provide for the closest approach of gel particles were given particular
attention in this investigation.

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FROM METAL-ORGANIC SOLS AND GELS

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PROBLEM STATEMENT

This project was designed to investigate those phases of the preparation process which affect transformation of alumina sols and gels to aluminum oxide bodies.

ABSTRACT

The process used to form monolithic transparent Al_2O_3 bodies from metal-organic starting materials at low temperature via the gel process involves essentially four steps: hydrolysis, peptization, gel formation, and pyrolysis. Each step has been systematically investigated by modification of associated variables in order to determine the combination of factors which produces optimum results. It has been found that the interparticle distance. that is, the extent of approach attained by colloidal particles, at the point of gelling is of critical importance in maintaining monolithicity during the gel-oxide conversion. Minimization of this distance not only reduces the amount of shrinkage necessary during liberation of organics, allowing the body to remain in one piece, but also appears to allow interparticle bond formation during drying and pyrolysis, possibly involving hydroxyl and alkyl groups. For this reason, the factors that provide for the closest approach of gel particles were given particular attention in this investigation.

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1. INTRODUCTION

Ceramic and glassy materials have been produced for some time
by various gel methods, providing products with interesting and useful
properties. For example, powders of molecular level homogeneity, important
in phase studies, were produced from inorganic salts.[1] In addition,
gel processes beginning with organometallic compounds and yielding high
purity sub-micron sized powders have been studied extensively.[2] These
powders, however, eventually must be subjected to the high temperatures
involved in sintering or melting in order to form non-particulate bodies.
Therefore, the development of a process which produced monolithic pieces of
amorphous oxide directly from the gel at low temperatures was a signi-
ficant step forward in ceramic and glass processing technology. Most of
the previous work which produced non-particulate bodies via gel processes
has been done in the silica system,[3,4] where production of a monolithic
piece is relatively straightforward because of the particular hydrolization
characteristics of the silicon alkoxides, which allow polymer chains in
the silanol gels to remain intact.[5] A transparent, porous bulk alumina
reported in 1974[6] was prepared from aluminum alkoxides. In this system,
the clear sol initially formed contains colloidal particles rather
than polymer chains and requires that certain different conditions be met[6-8].
The objective of this work was to investigate in detail the parameters
that contribute to the monolithic transformation of the alumina gel
system to an organic-free oxide system at low temperatures.

2. CONCLUSIONS

Conditions for optimum results in producing monolithic Al_2O_3 from metal organic starting materials have been determined:

1. Hydrolysis must be conducted in such a way as to yield peptizable species. For the alumina system, this requires that the hydrolysis product be in the form of aluminum monohydroxide, AlO(OH). Formation of the more stable aluminum trihydroxide, $Al(OH)_3$, must be prevented.

2. The formation of aluminum trihydroxide, or bayerite, can be prevented if: (a) the hydrolysis water temperature is above 80°C, (b) the initially formed amorphous aluminum monohydroxide by cold water hydrolysis is peptized before it has a chance to convert to trihydroxide, or (c) the initially formed monohydroxide is deprived of the water needed for conversion either by drying or replacing the aqueous medium with a non-aqueous one.

3. The alumina system can be peptized above 80°C with peptizing agents which do not form complexes with aluminum and are strong enough to satisfy charge requirements in small amounts.

4. The amount of peptizing agent added must be kept within a well-defined range. Best results are obtained when the electrolyte concentration causes the gel to attain minimum volume. For the alumina system, the acceptable range of electrolyte concentration has been experimentally determined to be 0.03-0.10 moles per mole equivalent AlO(OH) for strong electrolytes and 0.30-0.20 moles/mole for weak electrolytes. The optimum condition in both cases is 0.06-0.07 moles/mole, where the gelling volume passes through a minimum.

5. An aqueous medium is necessary to achieve peptization in the aluminum colloidal system.

6. The most effective method of gelation in the colloidal alumina system is to concentrate the system to the point where the peptizing electrolyte causes the sol to gel. Concentration involves removal of liquid by evaporation.

7. Transformation to an essentially organic-free oxide system requires a heat treatment up to 500°C. If the monolithic nature of the gel is to be retained during this transformation, drying and firing must be sufficiently slow to allow gases to escape without excessive pressure or stress buildup within the sample.

8. The resultant aluminum oxide from such a transformation is substantially transparent and porous. The porosity is of the order of 65% and is made up of pores whose diameter falls within a few angstroms of a mode diameter below 100 Å. These pores do not interfere with light transmission. It is found that the pore diameter can be changed by changing the suspension liquid.

9. Evidence suggests that, in colloidal systems, a smaller interparticle distance at the gelling point increases the capability of the gel system to retain its integrity. Thus, there is a critical interparticle distance which must not be exceeded if the gel is to remain monolithic during the conversion to oxide. For the aluminum monohydroxide investigated here, a minimum interparticle distance at the gelling point occurs with 0.25 g AlO(OH) per cc of gel. This is produced when the acid concentration is .06 moles per mole AlO(OH). Gels which contain less than 0.05 g AlO(OH) per cc at the gelling point tend to break up during conversion.

3. RECOMMENDATIONS

1. Colloidal oxide-forming systems other than the alumina system should be investigated.

2. Investigations should be conducted on the properties of non-colloidal oxide-forming systems, especially those properties related to the nature of the chemical bonds, degree of polymerization, and their effects on the capability of the system to transform to a monolithic oxide.
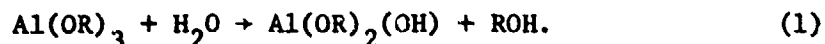
4. VARIABLES AND THEIR EFFECT IN THE PREPARATION PROCESS FOR MONOLITHIC TRANSPARENT ALUMINA FROM ORGANOMETALLICS

The most direct approach to a discussion of the variables in question is to describe each preparation step, including all related variables and their subsequent effects in chronological fashion. The four main steps to be considered are:

- Hydrolysis
- Peptization
- Gel Formation
- Pyrolysis (Fig. 1).

4.1 Hydrolysis

The process of hydrolysis begins with an aluminum alkoxide, $Al(OR)_3$, where R is an alkyl group C_nH_{2n+1}. Aluminum secondary butoxide, $Al(OC_4H_9)_3^s$, is liquid at room temperature and was used primarily in this work because of its commercial availability at a relatively low cost and because its volatility allows for easy distillation to very high purities. Other alkoxides, such as aluminum isopropoxide, aluminum mono secondary butoxide diisopropoxide, and aluminum tertiary butoxide behave in a similar manner. Hydrolysis of aluminum alkoxides have been described in detail elsewhere.[7] The process yields various aluminum hydroxides, depending on water temperature. Hot water ($\gtrsim 80°C$) must be used in order to produce a stable aluminum monohydroxide. If cold water is used, the resultant amorphous monohydroxide converts rather quickly to trihydroxide, bayerite, which cannot be peptized. Figure 2 illustrates that, after only ~7 h in cold water, the aluminum hydroxide is about 60 wt% bayerite. Initially, amorphous monohydroxide is produced in hot or cold water as follows:

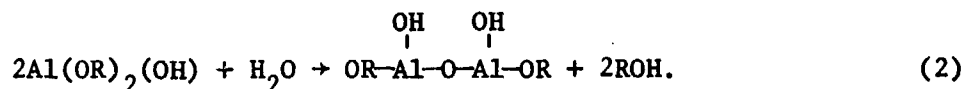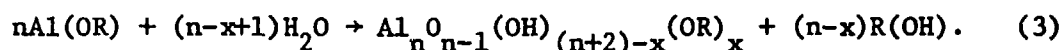$$Al(OR)_3 + H_2O \rightarrow Al(OR)_2(OH) + ROH. \tag{1}$$

CHEMICAL PROCESS

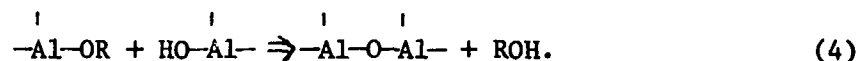FIG. 1 - Preparation steps in converting aluminum
alkoxide to monolithic Al_2O_3

OR groups continue to be lost as hydrolysis proceeds:

$$2Al(OR)_2(OH) + H_2O \rightarrow \underset{\substack{| \\ }}{OR}-\underset{\substack{OH \\ |}}{Al}-O-\underset{\substack{OH \\ |}}{Al}-OR + 2ROH. \qquad (2)$$

This reaction continues, eventually incorporating a large number of aluminum ions by a polymerization reaction which could be expressed by the overall equation:
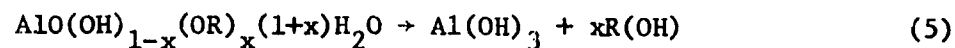
$$nAl(OR) + (n-x+1)H_2O \rightarrow Al_nO_{n-1}(OH)_{(n+2)-x}(OR)_x + (n-x)R(OH). \qquad (3)$$

"OR" groups in the hydrolysis product evidently play an extremely important role in this reaction. First, their presence in the monohydroxide appears to be directly related to the structural disorder required for the amorphous phase, since their removal from the amorphous hydrolysis product inevitably results in conversion to one of the crystalline phases. Secondly, their presence contributes to the dissolution of and eventual reaction with hydroxide groups of neighboring colloidal particles, causing an oxide bond formation between these particles and providing for continuity of the network, viz:

$$-\underset{|}{Al}-OR + HO-\underset{|}{Al}- \Rightarrow -\underset{|}{Al}-O-\underset{|}{Al}- + ROH. \qquad (4)$$

The effects of this phenomenon may be the reason why gels of colloidal systems produced from organometallic compounds, as opposed to those produced from inorganic salts for example, tend to retain their monolithic nature.

The concentration of OR groups in the monohydroxide is a function of water temperature and equilibrium conditions in the presence of alcohol in the mother liquor. Hydrolysis water temperatures below 80°C appear to cause retention of one out of every 20 alkyl groups in the structure; thus an amorphous monohydroxide is formed. This amorphous monohydroxide, if not peptized, however, is unstable in the presence of water and converts to aluminum trihydroxide.

$$AlO(OH)_{1-x}(OR)_x(1+x)H_2O \rightarrow Al(OH)_3 + xR(OH) \qquad (5)$$

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The OR groups promote dissolution of the amorphous material which then recrystallizes as bayerite after the elimination of OR groups by reaction (5). This preferred reaction will always occur at room temperature with aging. Conversely, raising the temperature of the system to 80°C or higher drives off OR groups suddenly, and bayerite cannot form because of kinetic restrictions. Under these conditions, immediate conversion to crystalline aluminum monohydroxide, boehmite, occurs. This does not require a stoichiometric change, and no transportation restrictions are involved.

$$AlO(OH)_{1-x} OR_x + xH_2O \xrightarrow{80°C} AlO(OH)(c) + xROH \quad (6)$$

amorphous monohydroxide + hot water → boehmite + alcohol

This reaction also requires a very small amount of water and, unlike the bayerite conversion, cannot be completely prevented by the denial of water (compare equations 5 and 6). It is this boehmite that is later peptized. Once formed, boehmite is stable and need not be stored above 80°C. Thus, hydrolysis is carried out by adding aluminum secondary butoxide to water which has been brought to 80°C. A preferred water/alkoxide weight ratio is ~100:1 because of the strongly exothermic nature of the reaction.

4.2 Peptization

This step is perhaps the most critical one in producing monolithic Al_2O_3 since a clear colloidal sol is formed at this stage. The precipitate formed by the hydrolysis of aluminum alkoxides contains large agglomerates of AlO(OH) particles; these particles individually are very small, having diameters below 100 Å.

Prior to peptization, the aluminum monohydroxide particles have a positive residual surface charge due to H^+ and are surrounded by adsorbed water whose molecules are oriented such that the negative pole is nearest the AlO(OH) particle surface. Beyond this layer are freely-moving water molecules forming a layer which extends outward to the point

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where the mean electrical charge is zero.[9] This diffuse area surrounding
each particle is known as the lyosphere. At this point, mass attraction
of neighboring particles is the dominating force. When an electrolyte
is added to the system, however, its ions become part of the electrical
double layer in the lyosphere. If the strength of the electrolyte is
sufficient, lyospheres begin to repel each other; repulsion increases
with increasing particle charge and thickness of the double layer.[10]

These changes occurring upon peptization are evident in the
appearance of the sample. During peptization the precipitate disappears,
and the slurry changes to a clear sol which scatters blue light. This is
illustrated in Fig. 3. The slurry (Fig. 3b), if dried, yields a parti-
culate material, but proper peptization (Fig. 3a), gelling, and pyrolysis
of the same product produces monolithic Al_2O_3. Sol particles have proven
to be extremely difficult to observe because of their small size; even
under high magnification, individual particles are not easily singled
out (see Fig. 4). Estimates of sol particle sizes from STEM data range
from ~25 Å to 100 Å, those in Fig. 4 being closer to 25 Å.

Peptization of the hydrolysis product requires:

● Prevention of trihydroxide (bayerite) formation.

● Addition of a critical amount of certain acids which will
  not complex with aluminum.

● Heat treatment above 80°C in an aqueous medium.

These conditions are, however, not sufficient to assure that
the resultant sol will yield monolithic oxide material. It is also
required that the amount of acid be kept below a critical value which
is related to its ionization constant; therefore this value is different
from inorganic and organic acids.[8] HCl, HNO_3, $HClO_4$, CH_3COOH, HCOOH and
Chloroacetic acids meet the conditions for peptization in the alumina
system since they do not complex with aluminum and are strong enough to
fulfill charge requirements in small amounts. Formic, acetic, tri-
chloroacetic, hydrochloric and nitric acids were used in this work.
Although peptization can be achieved at temperatures between 80 and 100°C,
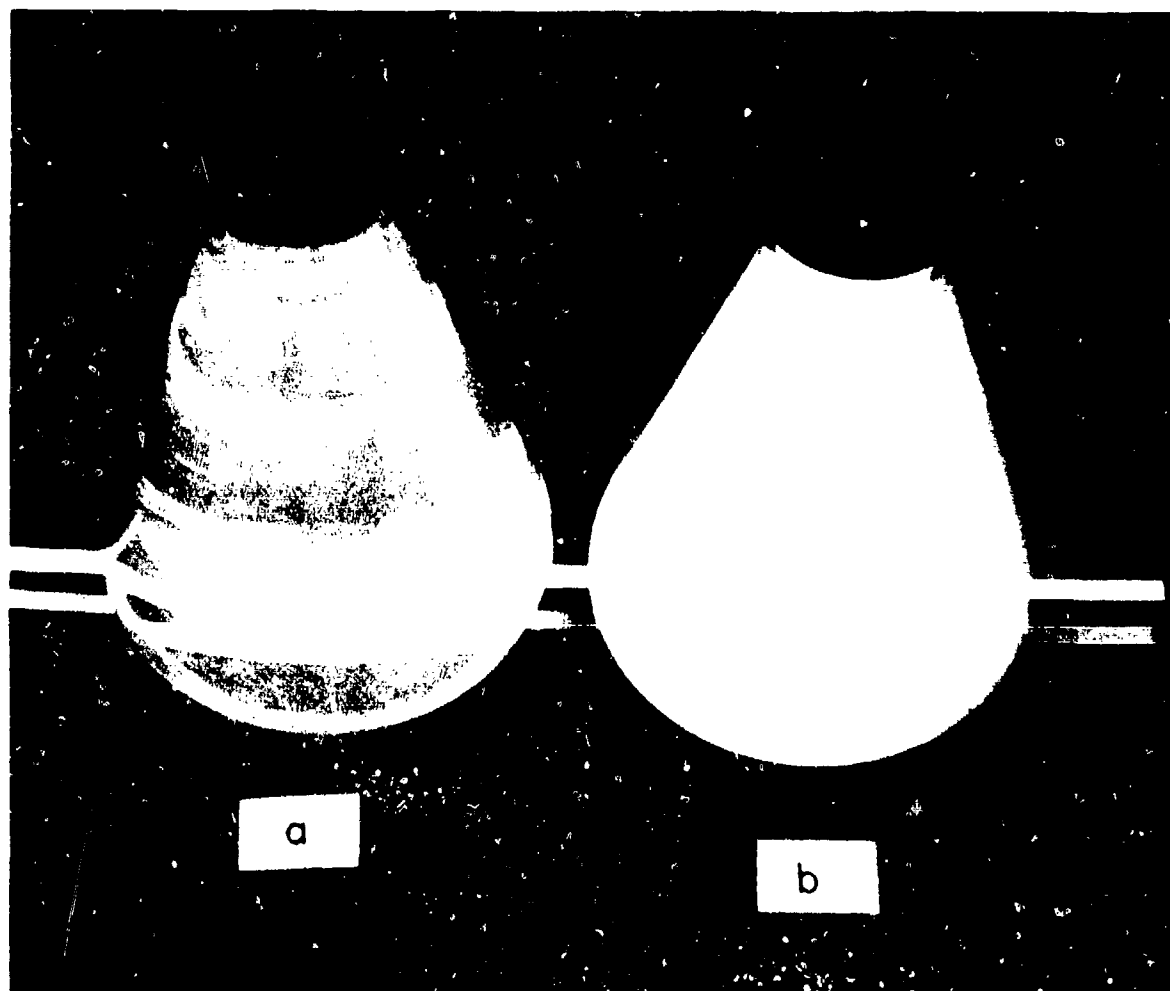temperatures at the higher end of this range are preferred because

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Fig. 3 – Effect of peptization on the appearance
of the liquid
(a) Properly peptized alumina sol
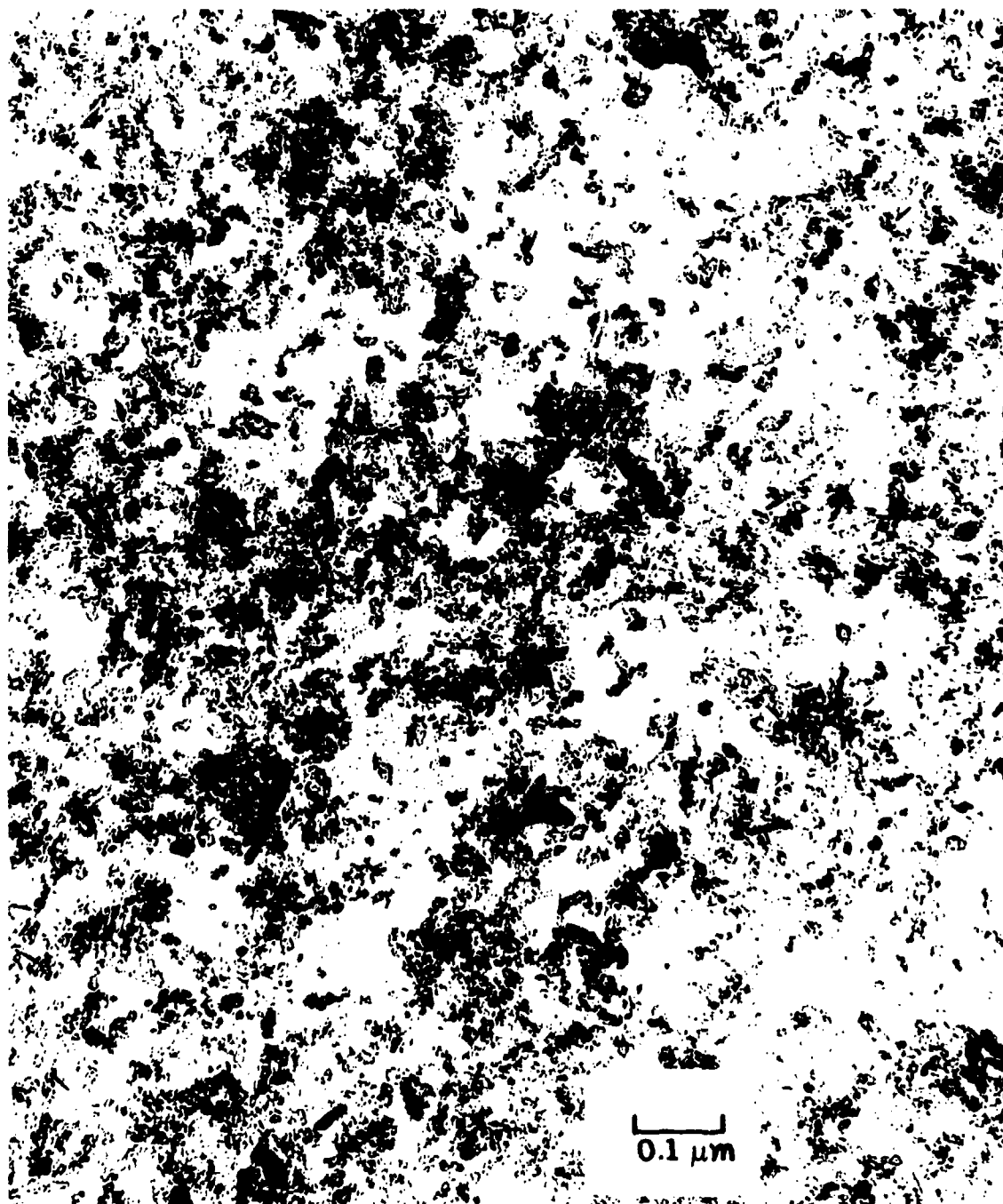(b) Opaque slurry of unpeptized alumina

Fig. 4 - Electron micrograph of AlO(OH) sol. The sol is prepared
by hydrolyzing one mole Al(OPr^i)$_3$ with 200 moles of water
at 75°C and peptizing the hydroxide with 0.04 moles of HCl.

peptization rates increase dramatically with temperature. For example, peptization which would take weeks if carried out at temperatures in the low 80's could be accomplished in a few hours at temperatures approaching 100°C.

When discussing the amount of acid used, it is necessary to adopt a measurement other than pH, because of the sensitivity required. The pH of a sol as a function of acid addition does not show any discontinuity in the range found to be important in this work (.03 - .02 moles acid/mole hydrate), as shown in Fig. 5. Therefore, moles of acid per mole of equivalent aluminum hydroxide has been chosen as the unit of acid concentration for this system. It has been determined that the minimum acid concentration required for complete peptization is .03 moles acid per mole $AlO(OH)$. Any acid concentration above this will peptize the slurry to a sol but, as noted above, only within certain ranges of electrolyte concentration does the gel made from the sol remain monolithic during transformation to an oxide.

The volume at which the system gels, or gelling volume, passes through a minimum with increasing acid concentration (see Fig. 6). The decrease to this minimum results from the addition of small amounts of electrolyte, which neutralizes the original surface charge of particles mentioned above, allowing the system to contract. This initial drop in gelling volume can only be produced with those electrolytes that peptize the system. The increase in gelling volume shown in Fig. 6 at higher acid concentrations is due to another mechanism and can be produced by nonpeptizing electrolytes such as NaCl after the sol has been peptized with a proper acid (see Section 4.3.1).

For the alumina colloidal system, it has been found that the gelling volume will decrease up to 0.06 moles acid/mole of hydroxide. This is true for both inorganic and organic peptizing acids, e.g., HNO_3, CH_3COOH. Gel volume is of critical importance here because the ability of the system to remain monolithic is inversely related to the gel volume; if the gel particles are too far apart, the disturbance they undergo during later drying and firing processes is so great that the material cannot remain intact. Furthermore, the greater separation of particles may inhibit the interparticle bond formation mentioned in Section 4.1.
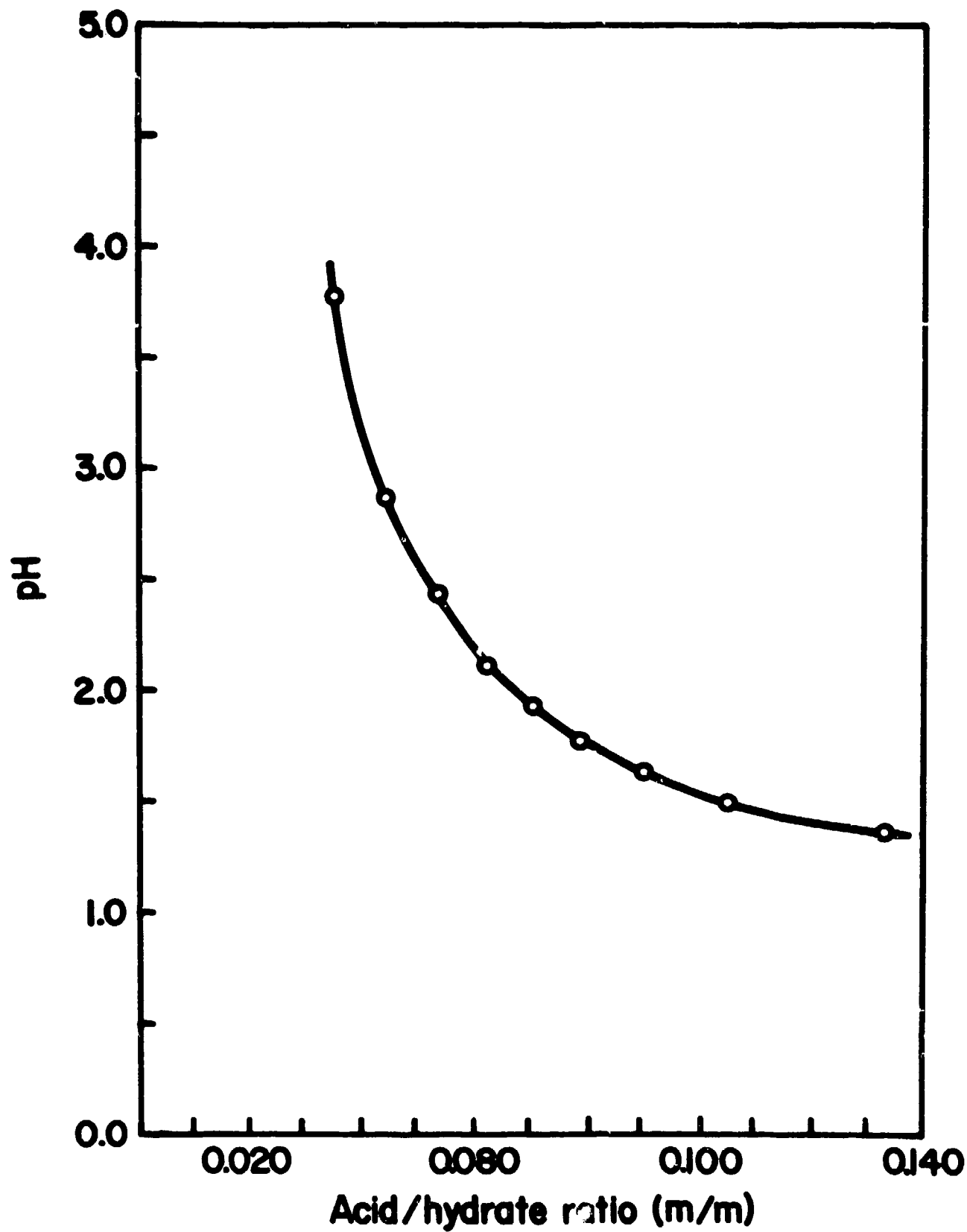
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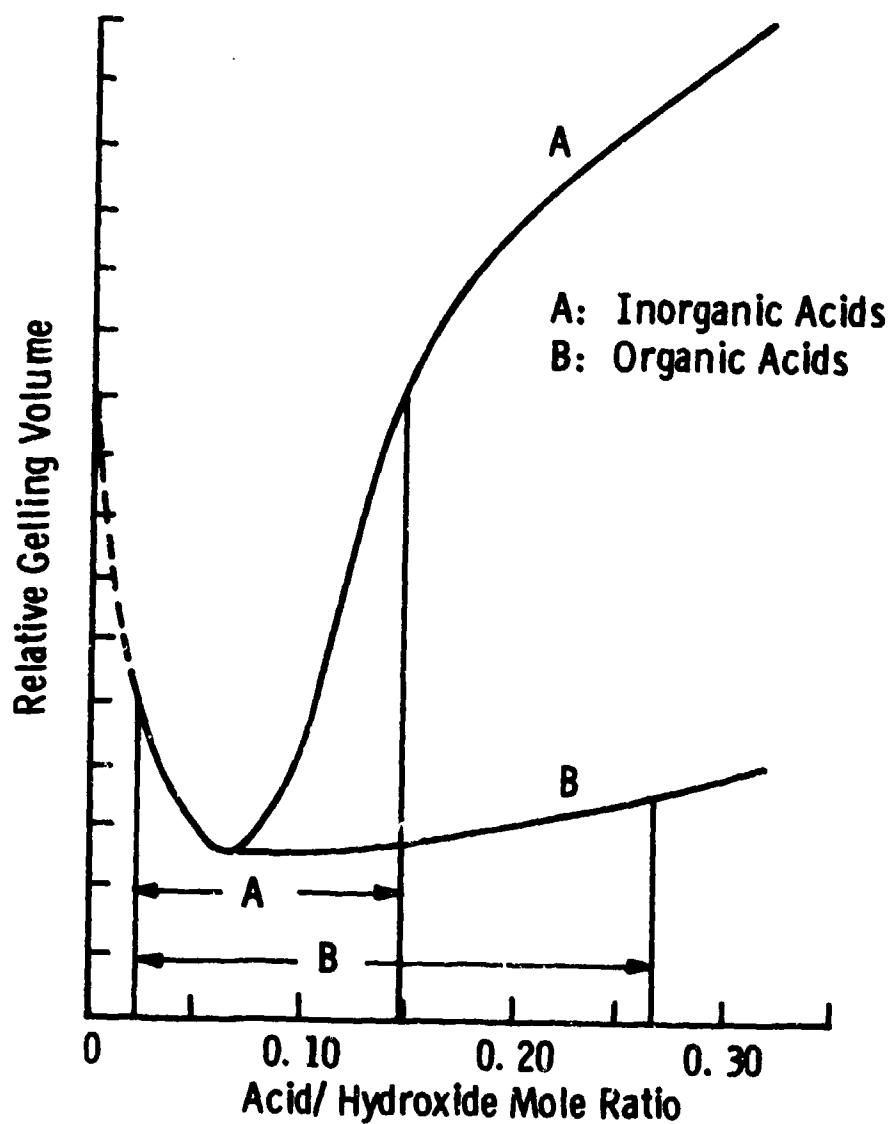Fig. 5 - Effect of acid concentration on pH of an alumina sol

Fig. 6 — Schematic representation of the effect
of acid concentration on gelling volume. Arrows
A and B indicate the range of acid concentration
for inorganic and organic acids, respectively,
which will allow a monolithic transformation
during pyrolysis.

A well-defined, sharp increase in the gelling volume occurs
for the inorganic strongly ionizing acids at concentrations beyond .06 -
.07 moles/mole hydroxide, and a more gradual increase is found for organic
acids at the same point. This suggests that an absorption of one ion
per 16-17 aluminum hydroxide molecules, AlO(OH), is the saturation point
of the peptization requirements. If excess charge is added, it increases
interparticle repulsion. Greater separation of colloidal particles
results, and the sol gels with a larger volume. At inorganic acid con-
centrations larger than 0.1 moles/mole hydroxide, gels lose the ability
to remain monolithic. This electrolyte concentration corresponds of a
gel volume where there is less than 5 grams AlO(OH) per 100 cc of gel.
As expected, larger amounts of organic acid can be tolerated before
a similar effect is observed, because they are weakly-ionizing electrolytes.
For example, as much as 0.2 moles of acetic acid per mole hydroxide can
be added without a significant gelling volume increase.

Experiments on the effects of acid concentration and aging
have yielded results as illustrated in Fig. 7-10. In these samples,
concentration to a gel was achieved by boiling off the water. Although
the initial amount of sol was the same for all samples in each group
and all samples contained the same amount of equivalent Al_2O_3, the
volume at which the system gelled varied with acid concentration.
These data exhibit the diminished overcharging effects characteristic
of organic acids, and Figs. 8-10 emphasize an additional phenomenon
observed for these electrolytes. If sols are gelled within a few hours
after peptization is completed, minimum gelling volume occurs at a higher
concentration than that found for inorganic acids due to slower dissocia-
tion. If sols peptized by organic acids are allowed to age, however,
the acid has sufficient reaction time, and minimum gelling volume occurs
at a concentration similar to that found for inorganic acids.

Figure 10 illustrates that trichloroacetic acid exhibits
behavior unlike other acids. The minimum gelling volume is attained
at higher concentrations, and aging seemes to reduce this volume at all
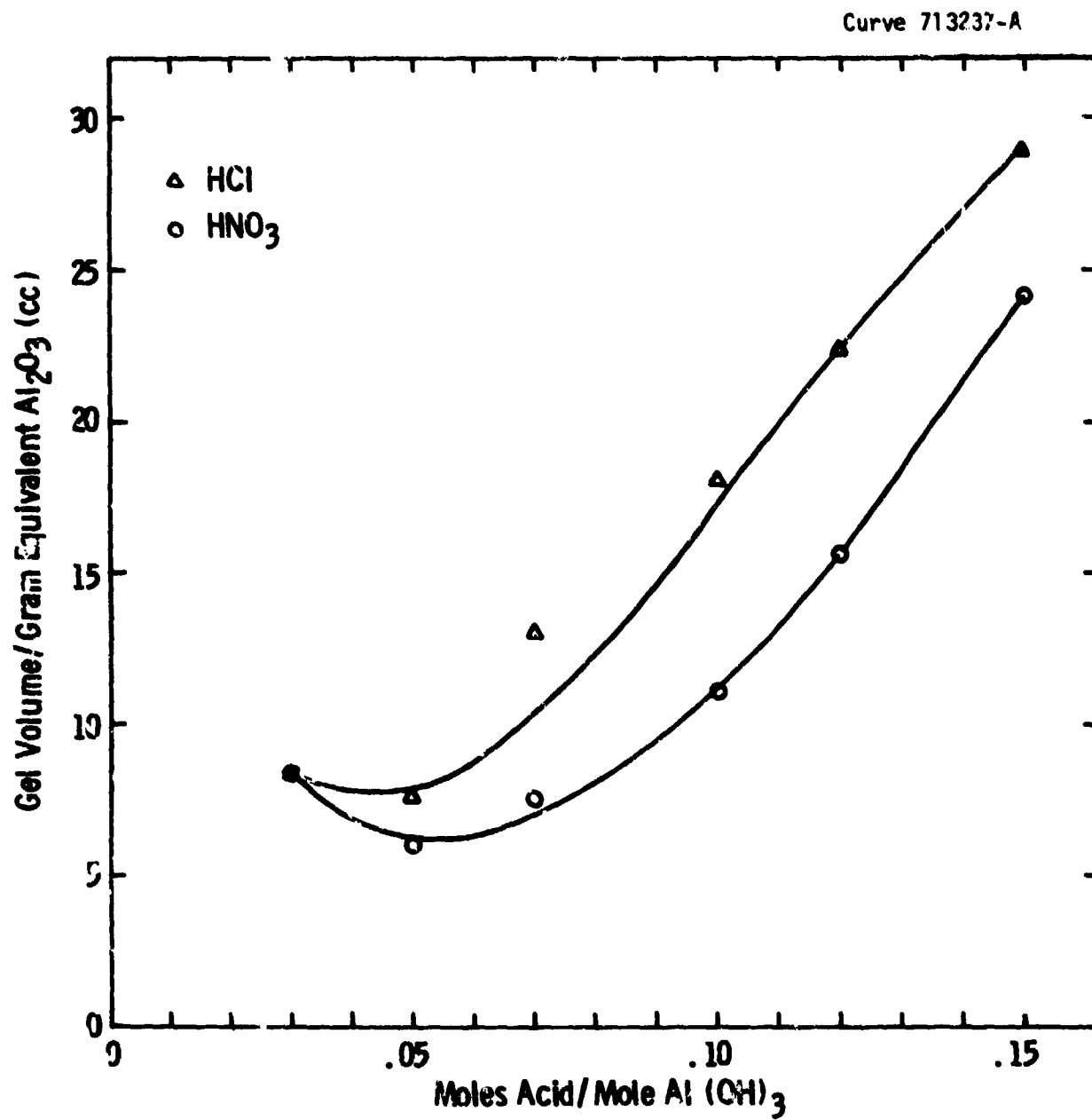concentrations. Higher gel volumes of non-aged samples may be partially

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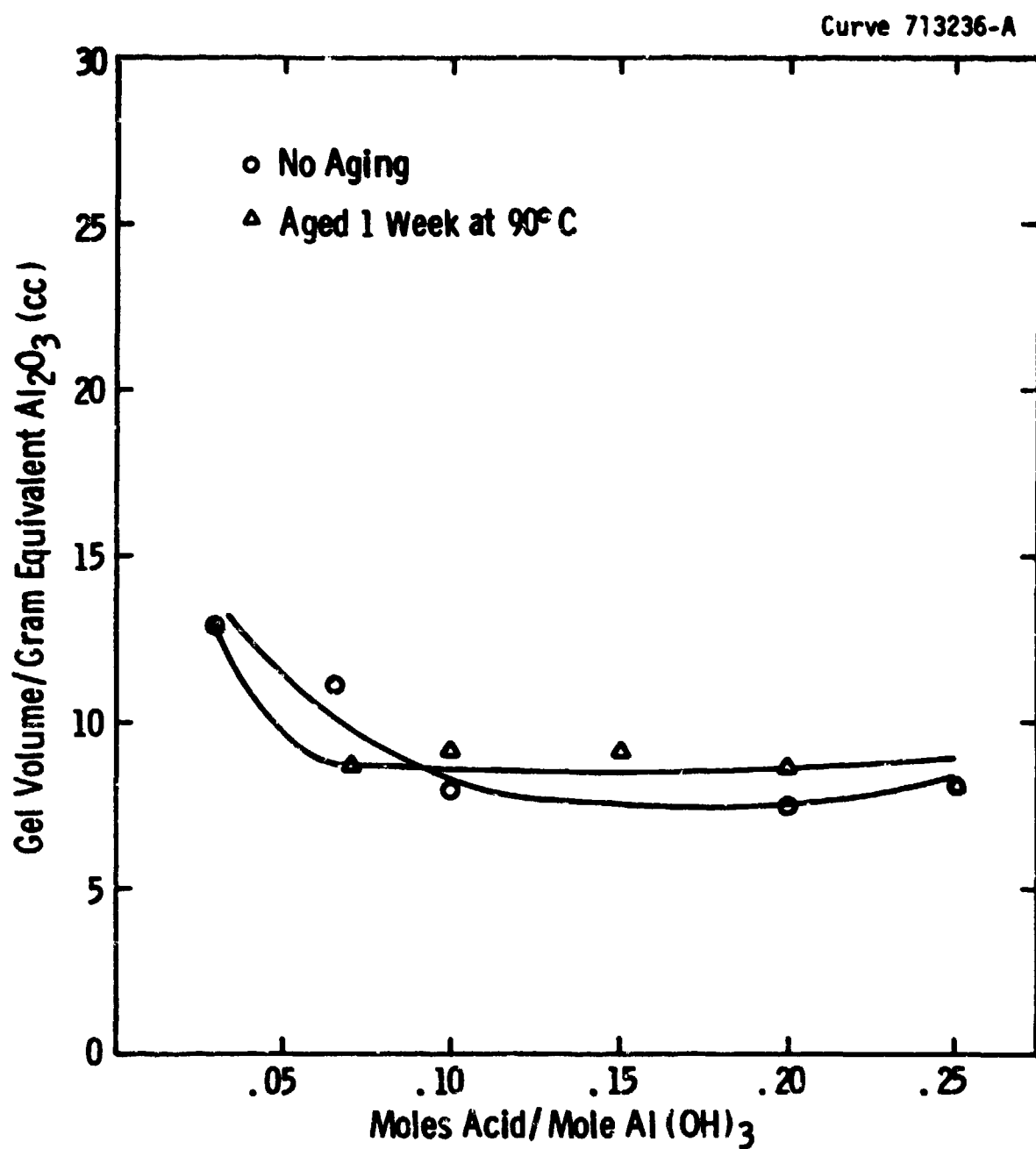Fig. 7 — Effect of inorganic acid concentration on gelling volume

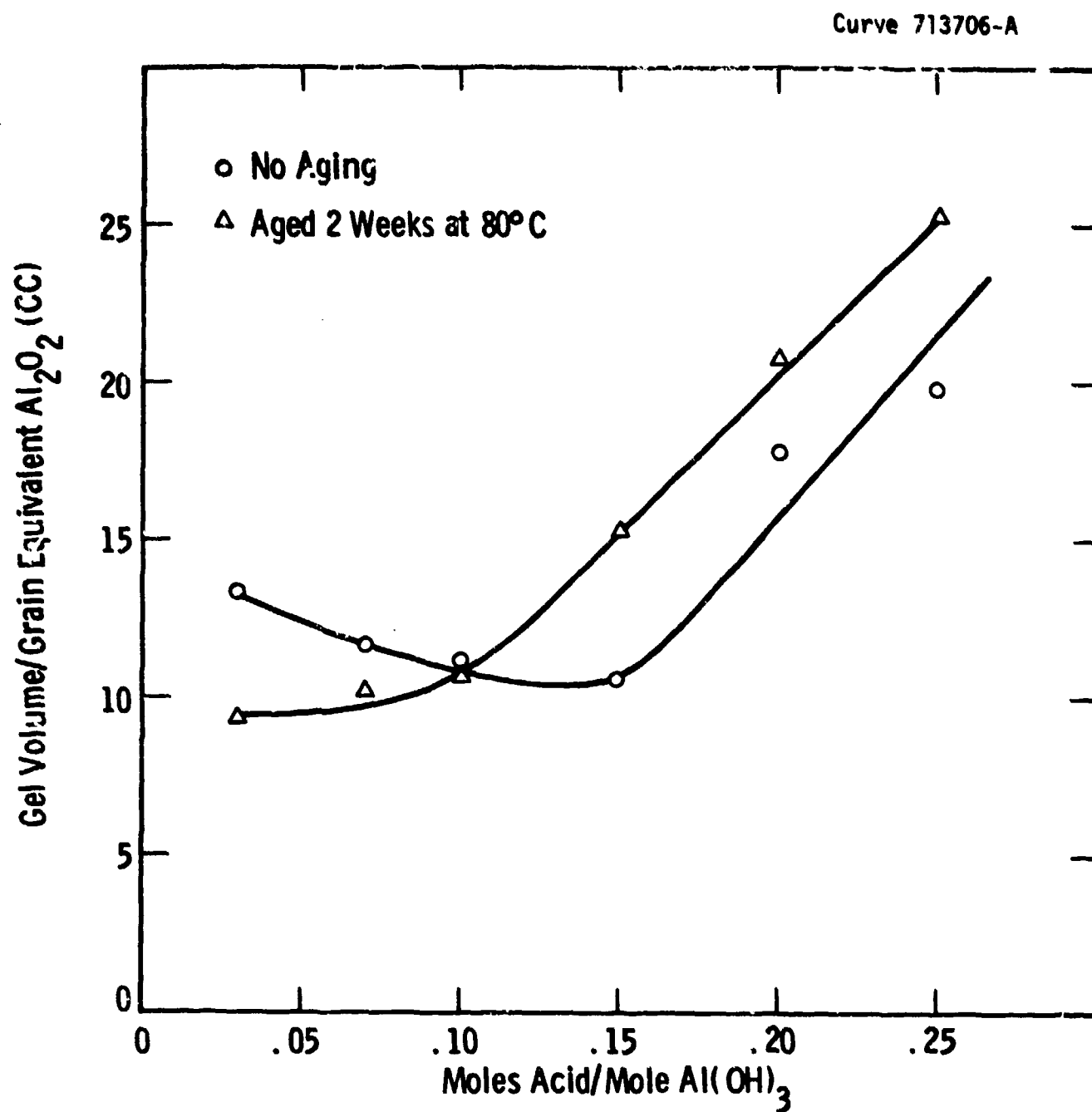Fig. 8—Effect of aging on the behavior of acetic acid

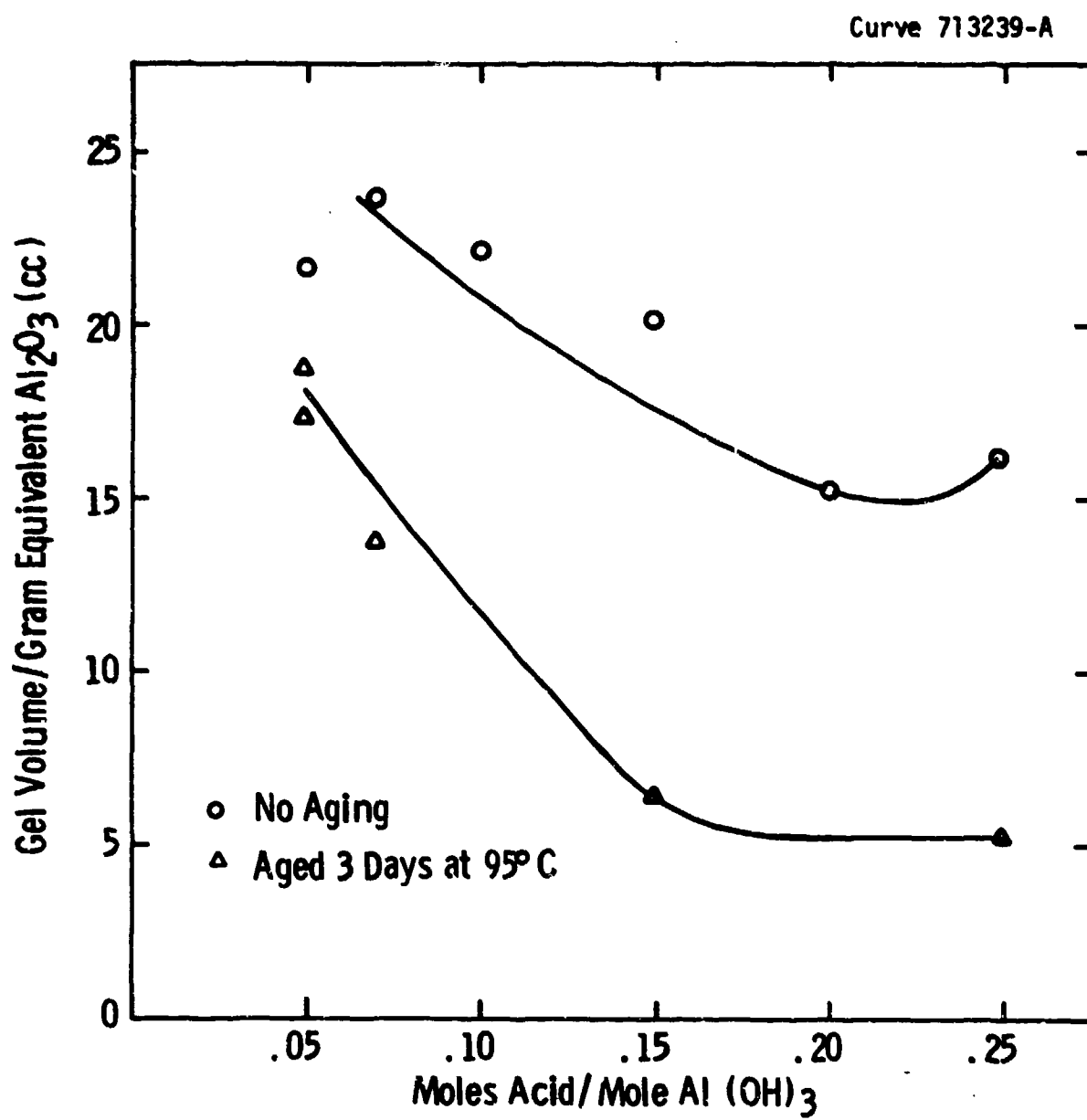Fig. 9 — Effect of aging on the behavior of formic acid

Fig. 10 — Effect of aging on the behavior or trichloroacetic acid

attributed to the fact that these samples foamed a great deal during the
boiling down process, and volumes were difficult to measure. It should
also be noted that these samples showed a greater tendency to remain
monolithic in the high-volume range than did high-volume samples ma.e
with other acids. However, their transparencies were reduced con-
siderably, except in very thin samples. This behavior warrants further
investigation.

In general, it may be said that gel volumes containing less
than approximately 5 g aluminum monohydroxide per 100 cc should be
avoided if a monolithic product is desired. Volumes of gels made with
organic acids show the least sensitivity to variations in acid concen-
tration, but the problem of carbon formation during pyrolysis (see
Section 4.4) may be encountered when they are used.

With these acids, however, a secondary effect enters into
consideration since they can be added in larger quantities. Without
raising the gelling volume, they tend to isolate colloidal alumina
particles in the gel by their physical presence in the interparticle
fluid when used in large quantities. This again prevents interaction
of colloidal particles and bond formation during drying. In this case
loss of the monolithic capability of the gel is not due as much to large
interparticle separation from electrical repulsion as to physical isola-
tion of each particle by a non oxide-forming layer. One conclusion of
this study is, therefore, that a critical interparticle distance in
colloidal systems must not be exceeded in the gel if it is to remain
monolithic during conversion to an oxide. This requirement alone, however,
is not sufficient to ensure successful conversion.

4.3 Gel Formation

In order to obtain a gel from a sol, the translatory motion of
colloidal particles must be arrested in the liquid medium. This is
accomplished when their lyospheres intersect,[12] which can be achieved
in various ways as described below.

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4.3.1 Method of Gelation

The primary method of gelling used throughout this work was simple concentration by boiling off the liquid components. In this method, removal of liquid medium allows the small lyospheres of the original sol to touch, and the interparticle distance in the resultant gel is minimized. This distance, as mentioned in Section 4.2, depends on the size of the lyospheres which, in turn, depends on the peptizing agent concentration. Removal of liquids may be achieved either by slow evaporation at room temperature or more quickly at or near the boiling point of water. This gelling method is advantageous because it is simple, rapid, and does not require the addition of materials. More importantly, however, it has proved to yield the best final material.

Another way of causing a sol to gel is to add a strong electrolyte to the system, increasing the replusion between lyospheres to the point where free movement is no longer possible. With this method, all of the liquid in the sol is retained in the gel, resulting in extraordinarily high gelling volumes, as shown in Fig. 11. It should also be mentioned that a small part of the high gel volume is attributed to the fact that strong electrolytes must be added in very dilute form, sometimes as dilute as 0.1 wt%, to avoid localized gelling in the area where a drop of electrolyte is added. Such localized gelling produces globules of gel in a liquid and homogeneity is so poor that gel volume is not meaningful. Note that electrolytes which were unsuitable for peptization because of complexing anions will work as gelling agents if they are strong enough to produce the desired effect in small amounts. Samples in Fig. 11 were first peptized with .07 moles of either acetic or nitric acid per mol AlO(OH). This peptizing acid was included as part of the total moles of electrolyte in the system. The data illustrates that, generally, the addition of strong electrolytes is not the preferred method of gelling, both because it produces high-volume gels which tend to break up upon heating, and because it sometimes involves the introduction of undesirable species such as sulphur into the system.
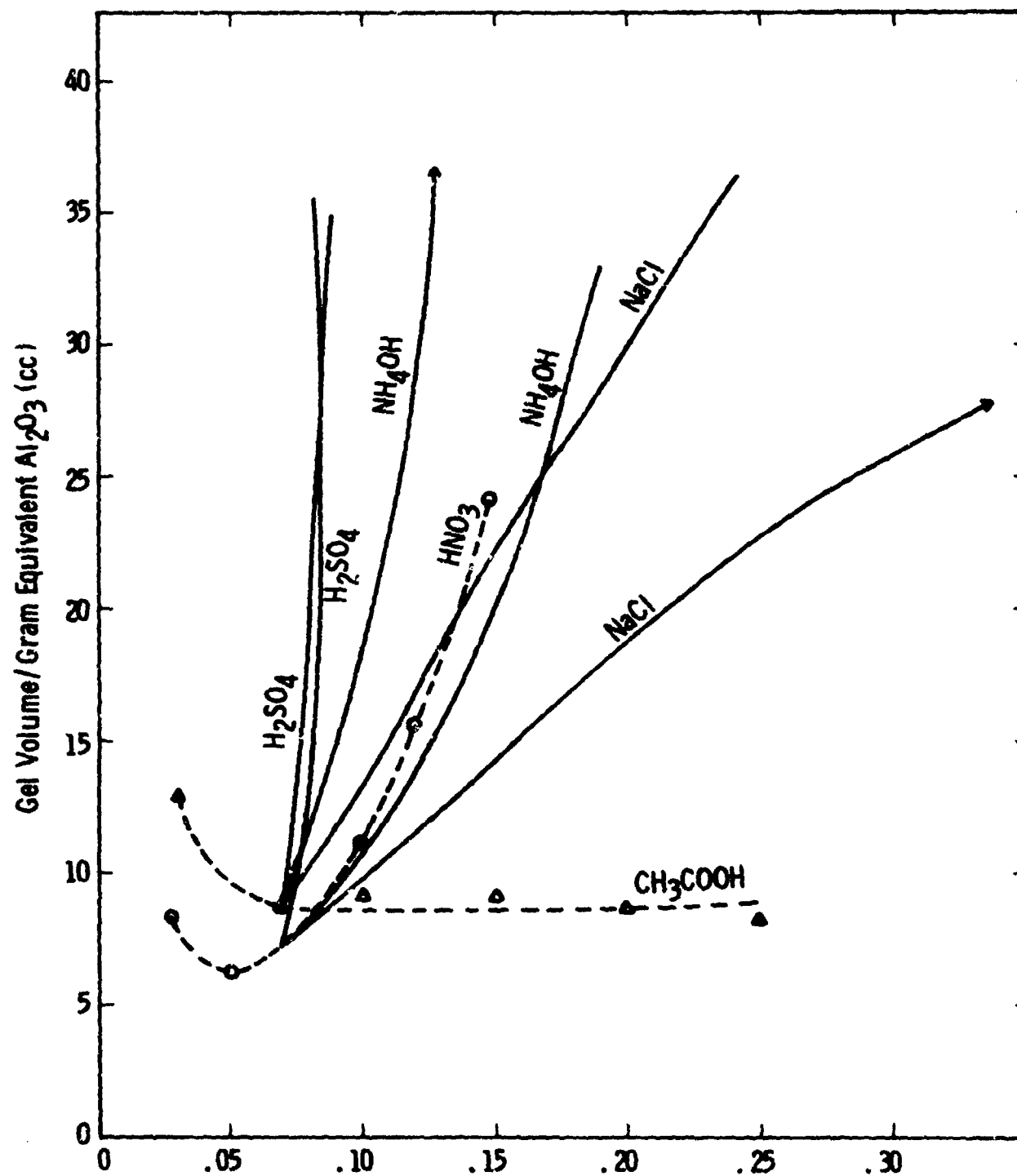
Fig. 11 — Moles Total Electrolyte/Mole Al (OH)₃

Gelling by electrolyte addition

A third method of gelation is aging. This occurs as a result of slow polymerization or cross bond formation between the particles. In general, the effect is small and is not observed unless some of the suspension liquid is removed. The sol concentration may be raised to 5-10 wt% equivalent Al_2O_3; lyospheres will grow with time, and the system may gel if left undisturbed for periods of days or weeks. This method, of course, leads to higher gel volumes. Figure 12 illustrates the difference in gel volume between samples gelled by aging and samples gelled by concentration as soon as peptization was complete. Real differences between gel volumes of these samples are diminished by the fact that samples must be concentrated to at least 5% equivalent Al_2O_3 before aging. A few samples of 5% concentration would not gel even after 1.3 yrs of aging.

4.3.2 Gel Medium

In the work described thus far, sols were prepared in an aqueous medium. Other experiments were done, however, using liquids other than water in order to investigate the effect of the gel medium on the final material. Even in these experiments, some water was needed for the formation of aluminum hydroxides from the alkoxides by hydrolysis. Samples were prepared in alcohols using only 3 moles of water per mole Al. The water and alcohol mixture was heated to 80°C, and Al sec butoxide was added in the proper amount. Butanol, ethanol and propanol were the alcohols selected for use. Aluminum monohydroxide particle formation was evidenced by the formation of a white, cloudy phase which settled out. Attempts to peptize the slurry to a sol were unsuccessful, however. This is presumably attributed to the fact that a conducting medium such as water promotes separation of charges, allowing for and even participating in the formation of the diffuse double layer around each colloidal particle.[9] This does not occur with alcohols.

An interesting phenomenon was observed when experiments were repeated using glycol instead of alcohol. No evidence of particle formation was observed upon the addition of Al sec butoxide to the glycol/water
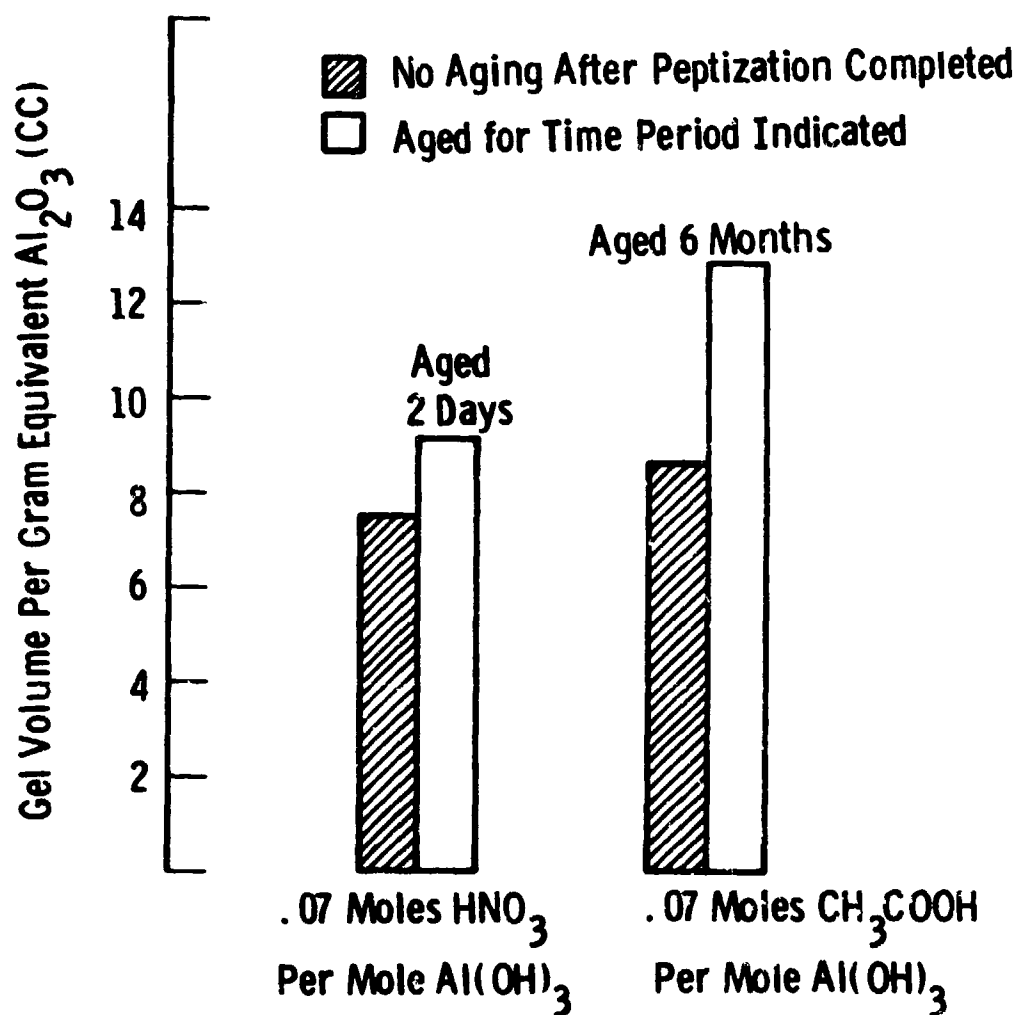
Fig. 12 — Samples peptized with nitric and acetic acids
were gelled by concentration (shaded columns) and by
aging (open columns). Aged samples were first
concentrated to 10 and 7 wt. % equivalent Al_2O_3,
respectively. Aging as a gelling method results in
retention of liquid and, consequently, higher gel volumes.

mix, but instead the sample remained clear. It is possible that a reaction between the aluminum compound and glycol inhibited or prevented hydrolysis; no change was observed even after the addition of large excesses of water.

Further attempts to incorporate alcohol into gels were made where the water was removed from aqueous alumina sols by boiling them down close to their gelling volume whereupon alcohols were added to the system. This method allows replacement of 70-80% of the water medium by alcohol. The alcohol-containing sols were later gelled by boiling or room temperature evaporation. They tended to produce observably clearer gels. The Al_2O_3 produced from these gels was very clear and glass-like in appearance and did not have the bluish, hazy characteristics of Al_2O_3 produced from aqueous sols. BET measurements showed that the pore size of this alcohol-based Al_2O_3 was noticeably smaller than that of water-based Al_2O_3. This is thought to be due to surface tension differences between alcohol and water. Perhaps more significantly, alcohols such as ethanol, C_2H_5OH, strip hydroxyl groups from the surface of colloidal particles, causing them to approach each other more closely, and possibly enhancing chemical bond formation. This area, again, must be investigated in much greater detail.

When glycol was used in the same manner, preliminary concentration was not necessary. Since glycol has a higher boiling point than water, samples were simply stored in an oven at 115°C for several weeks until the water boiled off. Some glycol was also lost during this storage in order to yield firm gels. It was found that, no matter how large the amount of glycol added, enough was lost so that all samples gelled at approximately the same volume, ~70 cc/g equivalent Al_2O_3 (see Fig. 13). When smaller amounts of glycol were added, gel volumes decreased proportionately. The lowest gel volume was attained, consequently, where no glycol was added. This case, again, represents a totally aqueous system. When acetic acid was used as the peptizing agent instead of hydrochloric acid, the characteristic volume was reduced from ~70 to ~23 cc/g equivalent Al_2O_3. Similarly, no advantage in gel volume over the aqueous system was produced in these samples.
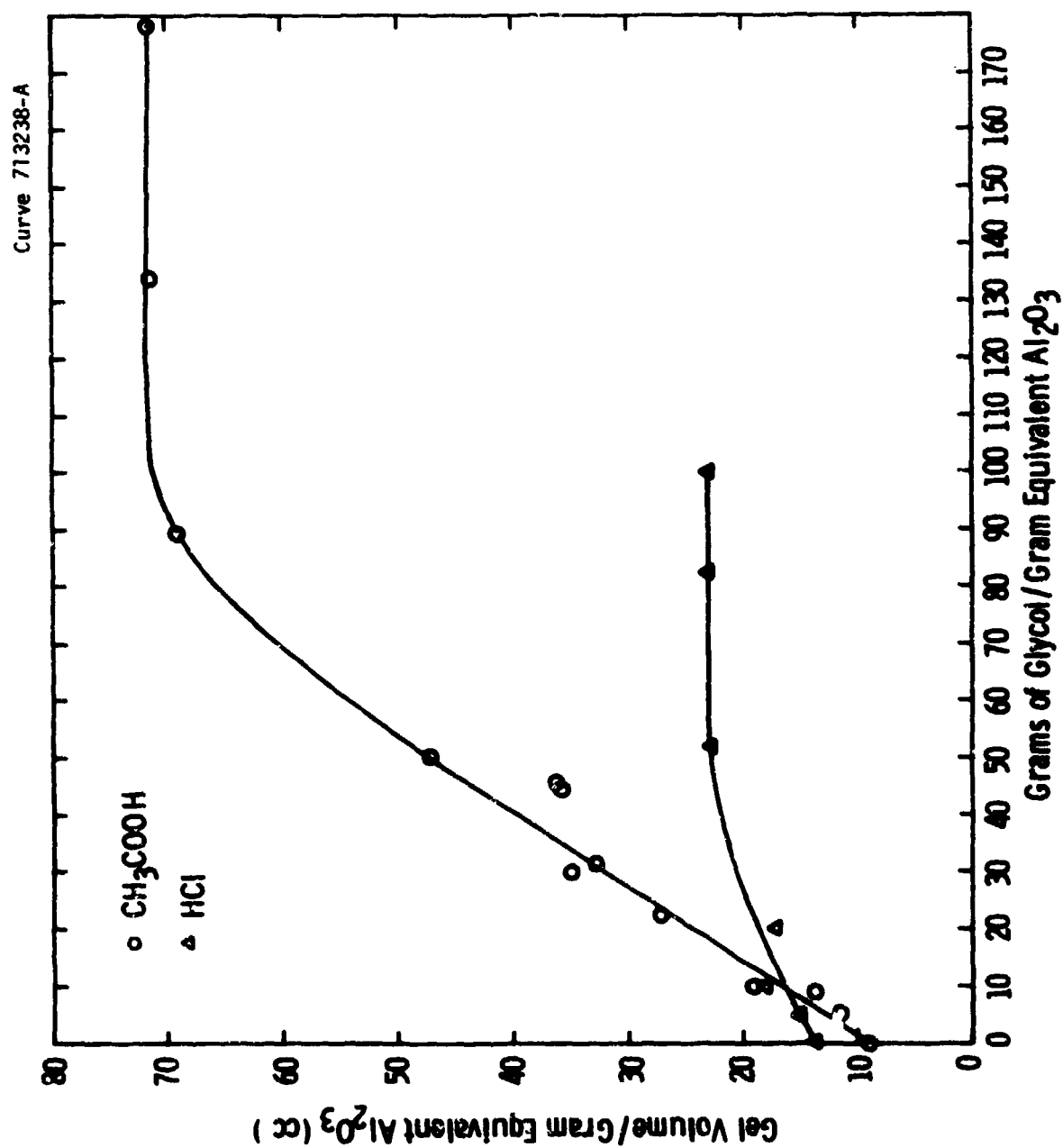
26

Fig. 13 — Effect of amount of glycol on gelling volume

Curve 713238-A

CH₃COOH
HCl

Grams of Glycol/Gram Equivalent Al₂O₃

Gel Volume/Gram Equivalent Al₂O₃ (cc)

Although glycol-based samples did not tend to remain monolithic in bulk during heat treatment, it was possible to produce coherent thin sheets of Al_2O_3 from these sols. This may be desirable in certain applications where pore morphology is of concern (see Section 4.5). The problem of carbon formation during heat treatment is encountered when glycol or glycerine is used as a medium. This problem was so troublesome in the case of glycerine that its use is not suggested. For glycol, however, the problem is easily overcome. (See Section 4.4 for details.)

4.4 Drying and Pyrolysis

Even in gels whose volume has been minimized by control of peptizing acid concentration, considerable shrinkage occurs during drying. A low volume gel will typically lose 35 to 50% of its volume during drying,[11] which is carried out at room temperature in a semi-closed container. Once shrinkage is complete, the gel will lose an additional 23 wt% as internal liquid is lost, causing the formation of pores. This release of liquid may be accelerated by a slow heating to ~90°C. The dry gel is similar in chemical composition to AlO(OH), and exhibits the X-ray diffraction pattern of transition aluminum hydroxides.

The dry gel is then heated to 500°C in air at a heating rate of ~10°C min^{-1}. As shown in Fig. 14, thermogravimetric analysis indicates that pyrolysis is essentially complete at 500°C.

In samples peptized with large amounts of acetic acid and in those containing glycol, pyrolysis to 500°C allowed some carbonaceous matter to remain, causing such samples to turn brown or black. This, of course, must be avoided where optical quality is important. Undesirable carbon traces may be removed by extending heat treatment to 700°C. In samples containing glycerine as a medium, the carbon-formation problem was very pronounced; samples remained black after heating above 900°C, and a thick, noxious smoke was emitted throughout heating. For this reason, no data on glycerine-based samples has been included.
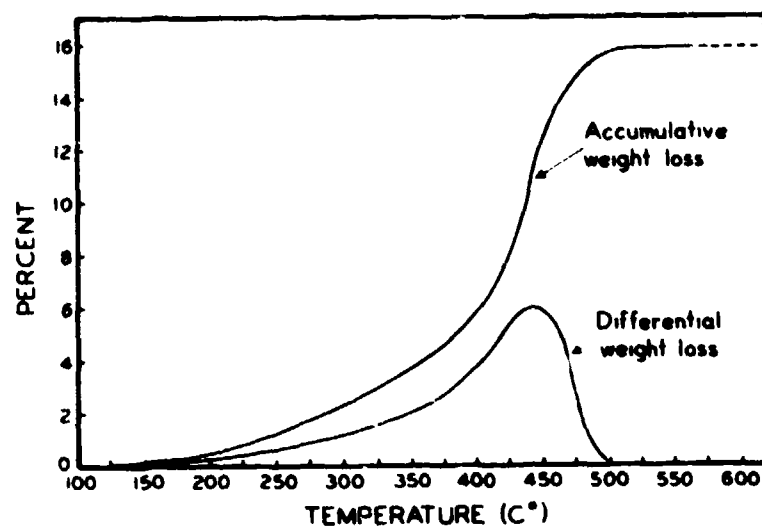
Fig. 14 — Weight loss during pyrolysis with a
heating rate of 10°C per minute.

4.5 The Final Material

The final product of the process described above is a transparent monolithic Al_2O_3 (Fig. 15) with an amorphous structure, as determined by X-ray diffraction. Porosity is 60 to 70%, yielding surface area values of 210 to 250 m^2/g. Figures 16 through 20 illustrate the difference in pore morphology between samples made from aqueous sols and those made from glycol-based sols. The main difference is that glycol samples possess a few very large pores not found in samples made from aqueous sols. Carbon formation in glycol-based samples requires heat treatment to temperatures higher than would otherwise be required, and this may affect pores, as may the release of larger organic groups. In any case, BET data indicates that most pores in all samples are below 40 Å in radius. These data also showed that the use of acetic acid as a peptizing agent (as opposed to HCl or HNO_3) produced samples slightly lower in surface area but slightly higher in total porosity. This suggests that the average pores are larger in acetic acid samples, which is verified in Figs. 16-20.

In high surface area materials, especially those produced from gels, retention of water in the final material is always of concern. The affinity of certain glass structures for water was emphasized in early work,[13] where large percentages of water were accommodated into glass structures using heat and pressure. It is, therefore, worthwhile to mention that, although high surface areas of samples prepared by the sol/gel technique may promote considerable absorbed surface water, infrared spectroscopy indicates that there is no significant concentration of hydroxyl ions in the structure. Indeed, the infrared absorption peak of OH in a silica glass prepared from a gel[4] was smaller than typical peaks found for commercially prepared fused silica.

Al_2O_3 produced by this gel method has several interesting and useful properties. The porous material has a higher optical transmission in the visible range than commercial polycrystalline Al_2O_3 of the same thickness. Also, its transmission increases with wavelength above ~450 nm.
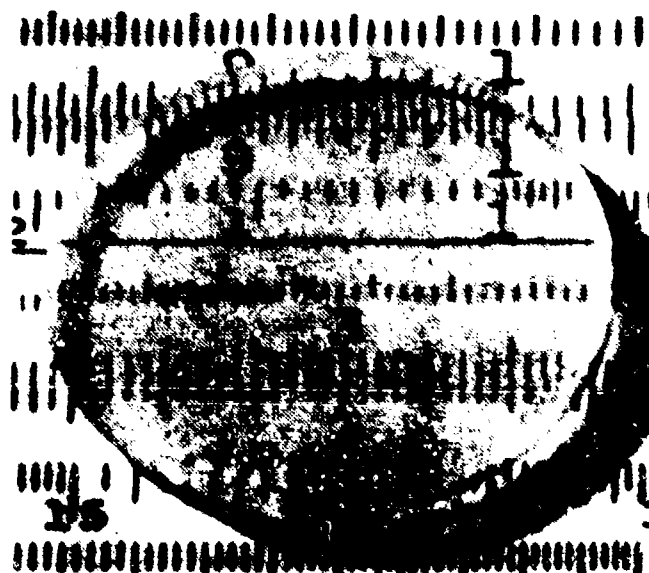
Fig. 15 - Al_2O_3 produced via the sol/gel method. This specimen is 65% porous after pyrolysis at 500°C.
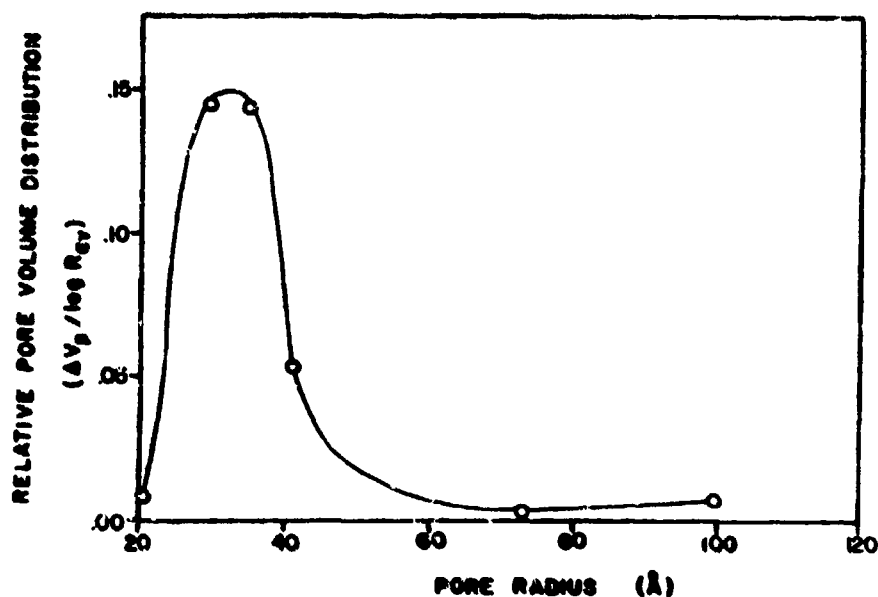
31

Fig. 16 - Pore size distribution of sample prepared in
aqueous medium, peptized with .07 moles acetic
acid per mole equivalent Al(OH)$_3$, and fired
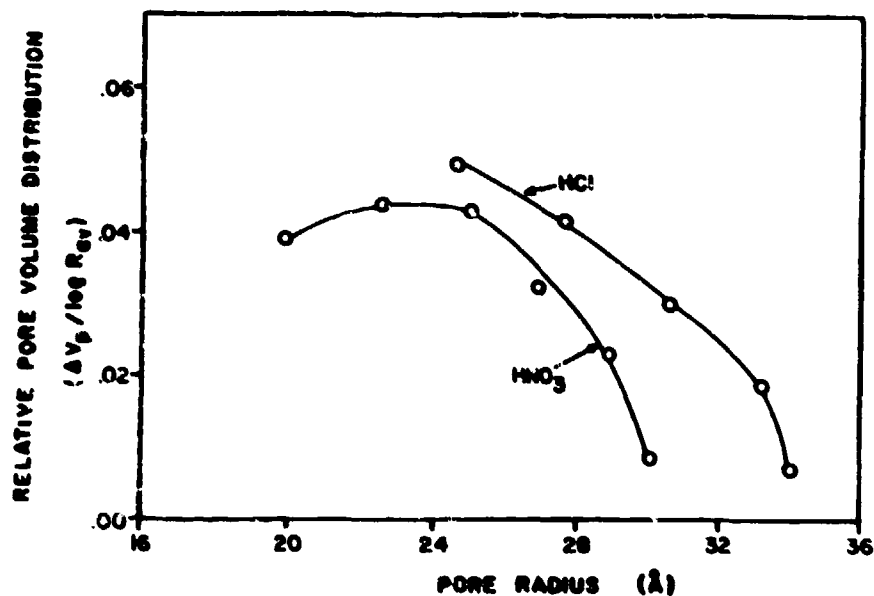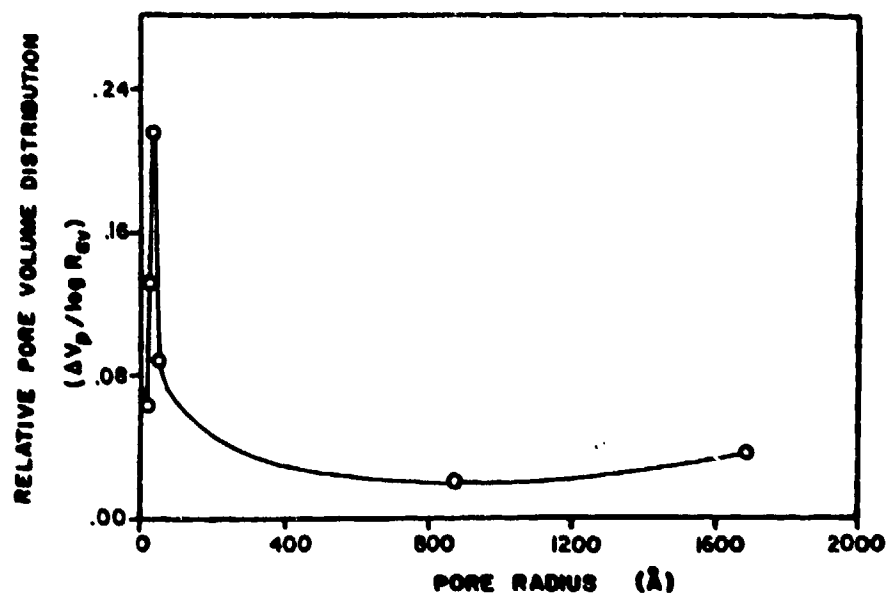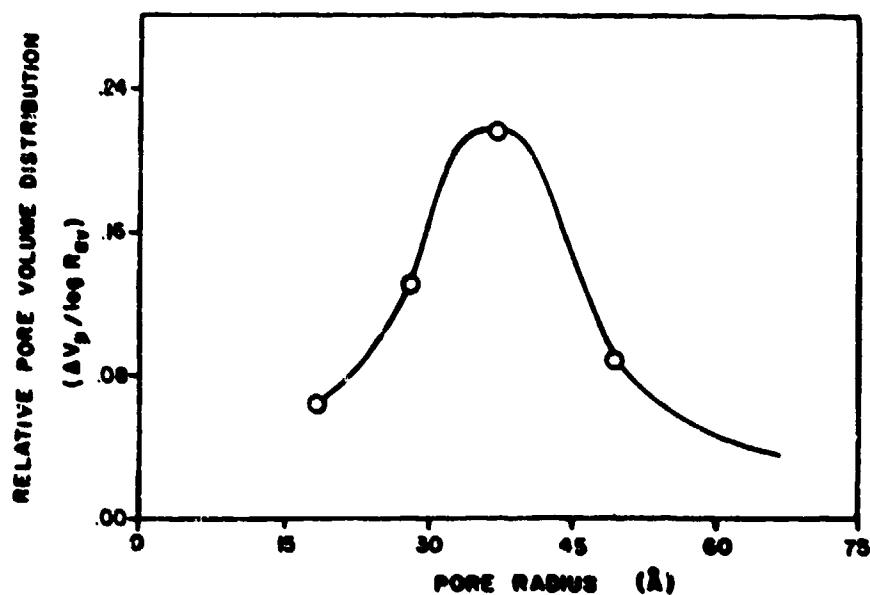at 500°C. Pore measurements were done using
the BET method.

Fig. 17 - Pore size distribution of sample prepared in
aqueous medium, peptized with .07 moles
inorganic acid per mole equivalent Al(OH)$_3$,
and fired at 500°C. Pore measurements were
made using the BET method.

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Fig. 18 - (a) Pore size distribution of glycol-based
sample whose gel volume had been ~23 cc/g
equivalent Al_2O_3. The initial sol was
peptized with .07 moles acetic acid per
mole equivalent $Al(OH)_3$, and the sample
was fired at 700°C. Pore measurements
were done using the BET method.
(b) Expanded peak from (a) indicates that
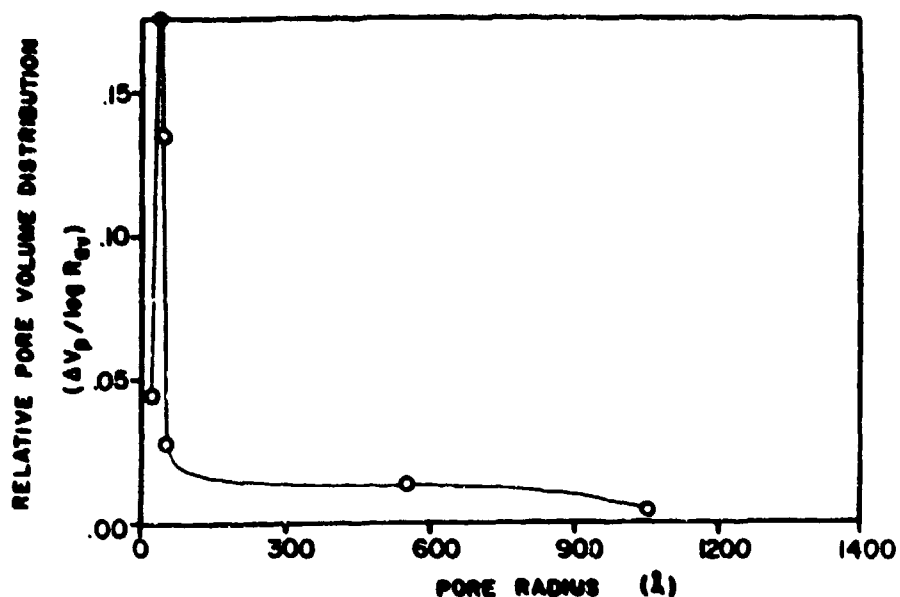the highest number of pores have radii
of about 35 Å.

Fig. 19 – Pore size distribution of a glycol-based sample whose gel volume had been ∿70 cc/g equivalent Al₂O₃. The initial sol was peptized with .07 moles HCl per mole equivalent Al₂O₃, and the sample was fired at 700°C. Pore measurements were done using the BET method.
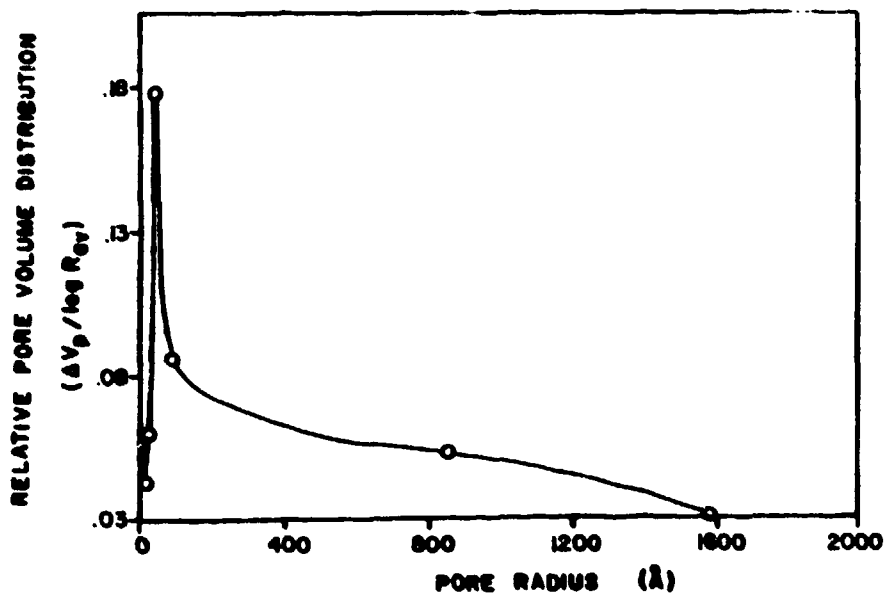

Fig. 20 – Pore size distribution of a glycol-based sample whose gel volume had been at the low end of the range (∿13 cc/g equivalent Al₂O₃). The initial sol had been peptized using .07 moles acetic acid/mole equivalent Al(OH)₃, and the sample was fired at 700°C. Pore measurements were done using the BET method.

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The high transmission is due to the fact that the size of pores is small
compared to the wavelength of light, thereby minimizing scattering.
The material also appears to be suitable for machining, again because
of large porosity. Although detailed investigations have not been con-
ducted, it shows high catalytic activity. The most immediate application,
however, may be in electronic, dessicant, and barrier coating technologies.
For example, this investigation has resulted in the development of a thin
film β-Al_2O_3 coating (Fig. 21) which is produced at relatively low tempera-
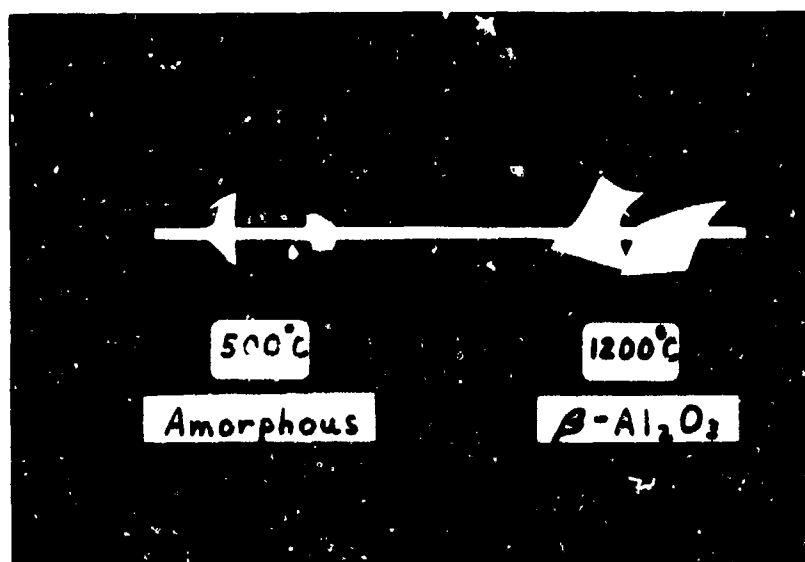tures for fuel cell application.

Fig. 21 - Thin film β-Al₂O₃ produced using the sol/gel
method. Firing to 500°C removes organic
components and yields a transparent amorphous
material; further heating to 1200°C allows
for the transformation to the crystalline
β-Al₂O₃ structure.

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